Report as of FY2009 for 2009RI80B: "Nanosilver-clay composite material as a reactive permeable barrier to control microbiological and chemical contamination in groundwater "

Publications

Project 2009RI80B has resulted in no reported publications as of FY2009.

Report Follows

Nanosilver-clay composite material as a reactive permeable barrier to control microbiological and chemical contamination in groundwater

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ABSTRACT

As are most natural resources, Rhode Island's ground water is both valuable and limited. Rhode Island's ground water resources supply drinking water to approximately 25% of the statewide population and as much as 100% of the local population in the southern and western portions of the state.

This one-year water quality project builds on the expertise of its team members and will directly benefit the people of Rhode Island by safely enhancing water supply from contaminated ground water resources.

This project will develop and evaluate a water filter made of a composite material. The composite material referred to herein is produced by combining local clay materials and silver nanoparticles. This filter will be designed primarily to treat microbiological contaminants such as *E. coli*, but will also be tested for its removal efficiency for inorganic and organic compounds. Iron and petroleum hydrocarbons present a current pollution quandary in Rhode Island and have been detected in many private wells in the state. The results of these tests will be used to design a water filter application suitable for use in private homes. This project builds on the previous work of this research team and carries the promise for future funding of subsequent extensions of this project.
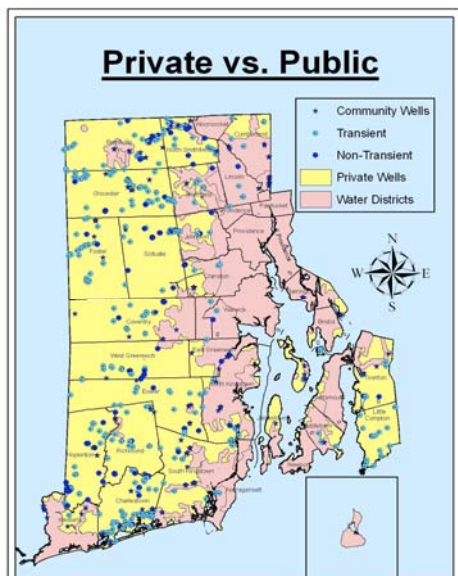
Figure 1. Geographical distribution of private owned wells in Rhode Island

KEYWORDS: silver nanoparticles, ionic strength, organic matter

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Rhode Island's population is supplied solely by ground water in approximately 25% of the state. In the southern and western portions of the Rhode Island as much as 100% of local populations are dependent on groundwater resources (Figure 1).

Groundwater is typically accessed via well and private well owners are responsible for the maintenance of their drinking water supply. Well owners need to ensure that the quality of their well water is fit for human consumption. Well water can be contaminated by biological, inorganic and organic compounds. The most common sources of well contamination are malfunctioning septic systems within the well catchment area, agricultural liquid waste infiltration, and inundation or infiltration of the well by floodwater.

If a private well becomes contaminated, households have several treatment options. However, current point-of-use technologies (e.g. reverse osmosis) tend to be expensive, difficult to operate and maintain, and/or may not be effective for removing the wide variety of pollutants potentially present in the groundwater. For instance, activated carbon filters very efficiently remove organic and inorganic compounds, but basically fail at the removal of bacteria.

To address this problem, we propose to develop a simple, cheap and locally manufactured water filter technology to be used as a point-of-use drinking water treatment alternative.

METHODOLOGY

Pathogenic microorganism quantification
Escherichia coli HCB 137 was used to create bacterial suspensions. This organism has been selected because it is a specific indicator of fecal contamination of water. The HCB 137 strain is non-pathogenic, i.e. its infective properties have been repressed. Bacterial-buffer solutions have been prepared as described by Oyanedel-Craver and Smith (2008), and aliquots have been added to synthetic water samples to obtain the desired bacterial concentration of approximately 10^8 cfu/mL.

Silver nanoparticles
Due to the current application of a commercial formulation of Ag-NP in some low-tech water treatments (i.e., ceramic filters by Potters for Peace), we have characterized and used Collargol™ (a silver nanoparticle product developed by Argenol Laboratories in Spain). Dynamic light scattering (DLS) was used to characterize the particle-size distribution of synthesized Ag-NP.

Column Tests
The following summarizes how the column systems have been characterized prior to amendment with Ag-NP. All column experiments have been carried out with water-saturated porous media. A known quantity of one of the three porous media was packed into a glass column (Kontex® or similar, volume: 25 to 75 cm^3). Teflon tubing and fittings were connected the columns to a precision piston pump (Acuflow Series I or similar). The porosity, pore volume (PV), and dispersion coefficient of each column was determined from the breakthrough curve of a conservative tracer, titrated water (Fetter, 1998) and the transport model CXTFIT 2.0. The flow velocity was held constant during each column experiment.

Column effluent samples were collected frequently and immediately analyzed using the analytical methods described previously. Effluent concentrations were reported as relative

concentrations, C/Co, where Co is the concentration of the solute entering the column and C is its effluent concentration at time t_n.

RESULTS

Characterization of nanoparticles at different water chemistry
Since several dissolved compounds are commonly found in natural waters, monovalent and divalent ions were used as background ions to test the effect of different water chemistries on the physical characteristics of silver nanoparticles.

Table 1 presents a summary of the values of average particles' size for silver nanoparticles. It can be observed that at the concentration tested in this study the average size of the particles does not change considerably. Silver nanoparticles can be synthesized using a variety of techniques, including electric spark discharging methods (Der-ChiTien et al. 2008), irradiation methods (Long et al. 2007), and chemical reduction methods (Soukupova et al. 2008). The most common manner of synthesis of silver nanoparticles is the chemical reduction of a silver salt solution by a reducing agent, such as borohydride, citrate, ascorbate, or a reducing sugar (Soukupova et al. 2008). The size of the particles can be manipulated using various reducing agents in the reaction. For example, using disaccharides as a reducing agent yields a smaller particle size than using monosaccharides (Soukupova et al. 2008).

The nanoscale sizes of these particles leads to a large surface area per volume ratio, such that a large percentage of atoms are in immediate contact with the solution and thus are readily available for reaction. In addition to the different shapes and sizes that can be manufactured, the surface of the nanoparticles can be modified using different agents; this process is called functionalization or capping. Capping agents are used in the synthesis process to prevent nanoparticles from aggregating and to obtain a range of small particle sizes. Olenin et al. (2008) determined that agglomeration was caused by high surface energy and thermodynamic instability of the nanoparticle surface. Capping agents interact with the surface of nanoparticles through electrostatic repulsion forces caused by surface charge, steric stabilization, or both (Sun et al. 2005; Guo et al. 2008). The most common capping agent used for the manufacture of silver nanoparticles is citrate (50%), followed by polyvinylpyrrolidon (20%), amines (10%), amides (5%), cetyltrimethylammonium bromide (5%), and others (10%) (Tolaymat et al. 2010).

Polyelectrolytes, surfactants, amines, and sugars are used to functionalize the surface of nanoparticles (Sen et al. 2006). These compounds increase the surface charge of the particles and provide electrostatic repulsions between particles to minimize aggregation and prevent the attachment of particles to surfaces (Sun et al. 2005). In addition to the electrostatic repulsion forces, high molecular weight organic compounds adsorbed to the nanoparticles surface can induce steric repulsion. To be effective, a thick and dense layer of adsorbed organic compound is employed to overcome the van der Waals attraction between the particles. The combination of electrostatic and steric repulsion (electrosteric repulsion) tends to be quite strong and long-ranged, and is known to be robust even at high ionic strengths.

Table 1. Effect of different ions dissolved on the average size of the silver nanoparticles

Concentration (mg/L)	Average particle size distribution (nm)		
	NaCl	*Ca(NO3)2*	*KNO3*
50	101	99	111
100	97	110	92
250	80	115	93

Some change, although not significant, was observed on the average particle distribution of the silver nanoparticles in the range of dissolved salt concentrations used. Figure 1 relates the particle size distribution of silver nanoparticles suspended at different concentration of salts. It can be observed that bigger particles are formed at higher concentrations, however, it seems that the number of these particles is not high enough to increase the overall average particle size distribution of the nanoparticles suspension. Below, Figure 2 quantifies the effect that different concentrations of dissolved compounds has on the particle size distribution of silver nanoparticles.
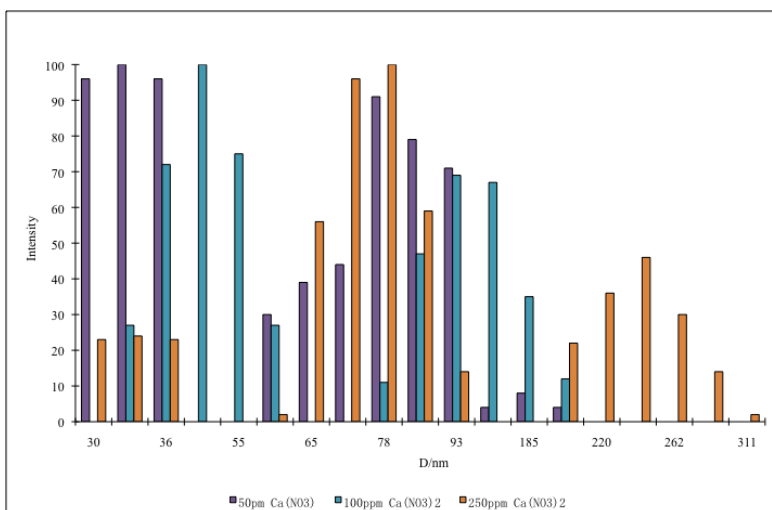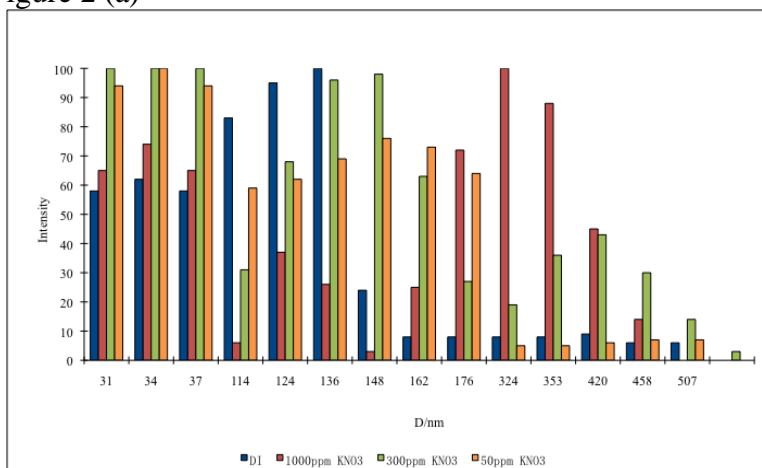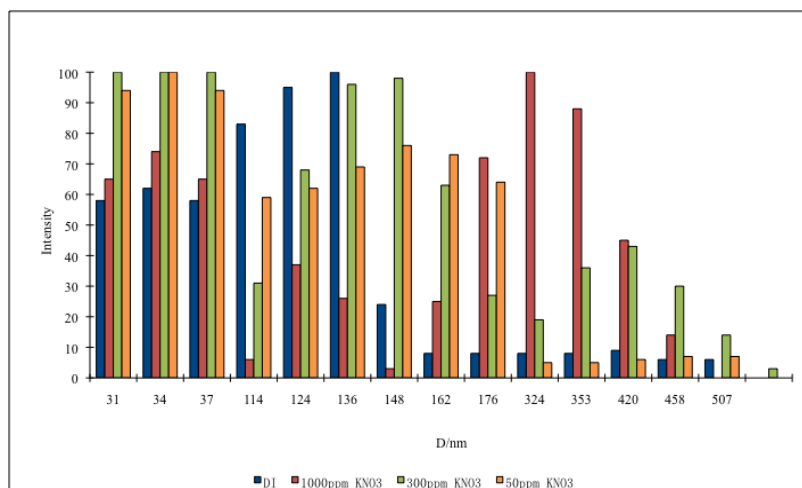

Figure 2 (a)

Figure 2 (b)

Figure 2 (c)

Figure 2. Effect of different concentration of dissolved compounds of the particle size distribution of silver nanoparticles (A) NaCl, (B) Ca(NO3)2 and (C) KNO3.

The storage time of silver nanoparticles in a liquid solution did not seem to have a significant effect either in the particle size distribution or the overall average particles size as it is presented in Figure 3.
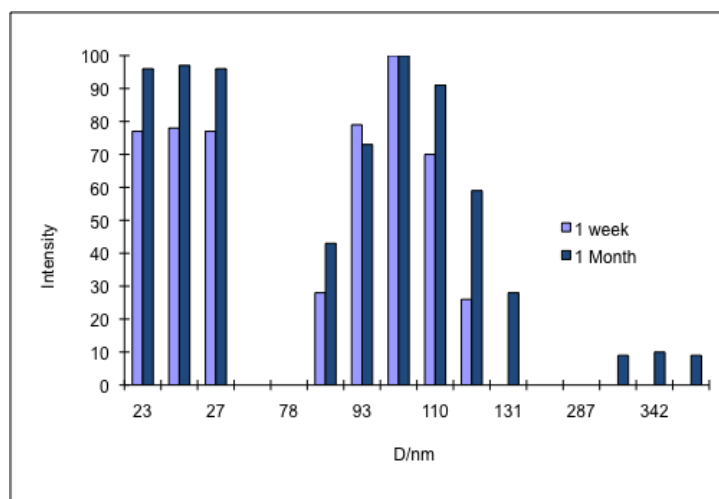

Figure 3. Effect of storage time on the particle size distribution of silver nanoparticles

The disinfectant performance of silver nanoparticles was also determined as a function of time. Figure 4 shows the summary of the different tests performed within the scope of this project. The figure shows that after a week of storage in liquid solution silver nanoparticles lost less than 2% of their original disinfectant properties.
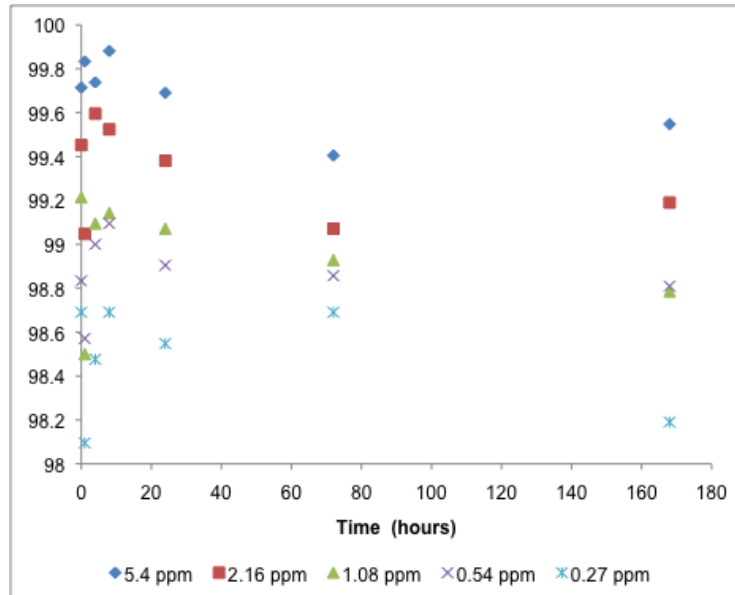
Figure 4. Disinfection performance as function of time.

Column experiments

The column tests were performed using Ottawa sand to determine the bacteria and nanoparticle retention in porous media. The retention of bacteria cells in the sand matrix have been extensively studied by other researchers. Figure 5a presents the breakthrough curve of the tracer (NaCl) and E. coli. Approximately 50% of the bacteria were retained inside the column. This result agrees with other studies found elsewhere. Figure 5b shows the breakthrough curves of the tracer (NaCl) and silver nanoparticles. Silver nanoparticles are proven to be slightly retained (about 2%), most likely because of their small particles size and low charge. Since Ottawa sand has a low charge, surface to surface interaction was expected in a low rate.
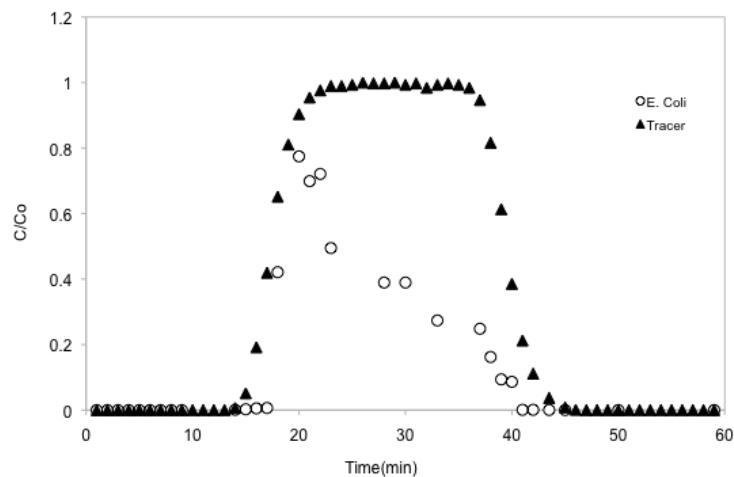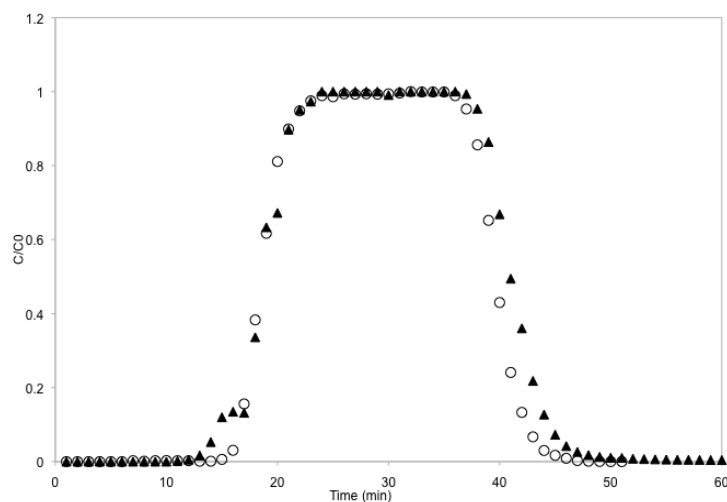

Figure 5 (a)

Figure 5 (b)

Figure 5. Breakthrough curves (A) Tracer and bacteria and (B) Tracer and silver nanoparticles.

CONCLUSIONS

The effect of various dissolved compounds as well as the storage time did not have a significant negative impact either on the physical properties or antibacterial performance of the silver nanoparticles. Therefore, silver nanoparticles are a potential suitable amendment to enhance antibacterial properties in porous media.

Sand type materials are not appropriate for the immobilization of silver nanoparticles due to their low surface charge reducing the possible interactions with the nanoparticles.

FUTURE WORK

Future research is necessary to determine the effectiveness of other types of porous media for filter technology. Materials with different characteristics such as higher cationic exchange capacity and higher organic matter content should be explored for this use.

Additionally, the implementation of different surface modifications to alter the silver nanoparticles surface must be studied in order to increase surface interactions with porous media.

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